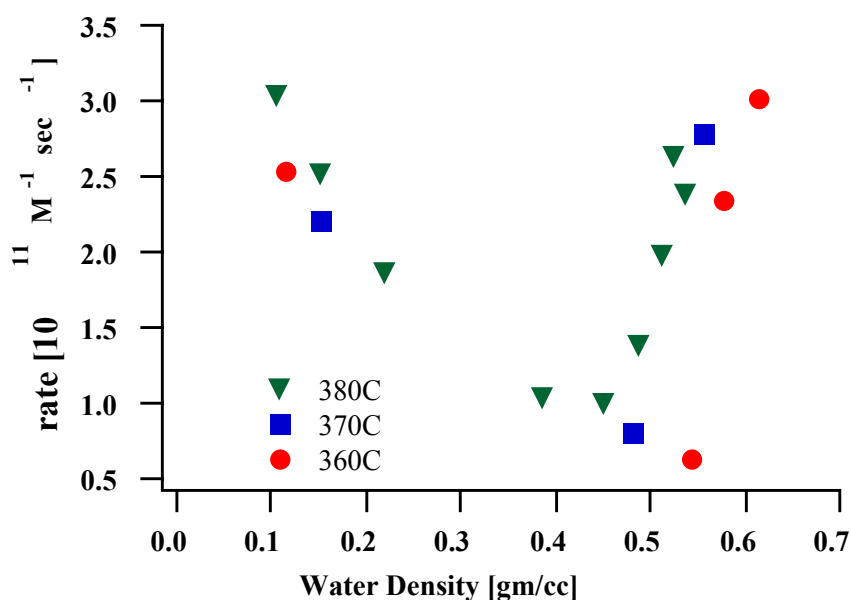


Effect of "Negative Hydration" on reactions in supercritical water

David M. Bartels and Charles D. Jonah

Researchers in the Argonne Chemistry Division have found evidence for "negative hydration" behavior in the reaction of hydrophobic solutes with ionic species in supercritical water. The study has been undertaken in order to assess the feasibility for higher temperature, more efficient nuclear reactors cooled by supercritical water ($T_c=375^\circ\text{C}$, $P_c = 220$ atm). Using picosecond pulses of ionizing radiation from an electron linac to fragment supercritical water, reactions of solvated electrons with O_2 and SF_6 , and the reaction of H atoms with OH^- were all measured as a function of the water density. At water densities between 0.6 g/cc and 0.4 g/cc, reaction rates decreased dramatically. The explanation seems to be that the water solvent clusters around the hydrophilic ions, but repels the hydrophobic molecules, to produce a large "potential of mean force" barrier for the reactions. A large solvent barrier is not present in the high density liquid phase. At much lower density the rate constant increases again, presumably because there are fewer water molecules to present a barrier. So-called "local density enhancements" have been investigated for some years in supercritical fluids, but this represents the first demonstration of an effect of "negative solvation". The results emphasize the great difference in radiation-induced reaction rates and mechanism which can be expected in the compressible supercritical regime relative to high density liquids.



Rate constants for the scavenging of solvated electrons by oxygen in supercritical water. The drop in rate near 0.5g/cc seems to be a general phenomenon in reaction of hydrophilic ions with hydrophobic molecules.